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Precise compositional analysis of styrene/butyl acrylate/methacrylic acid terpolymer by two-step reactive pyrolysis–gas chromatography with tetramethylammonium acetate

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ABSTRACT

Compositional analysis of a styrene (St)/butyl acrylate (BA)/methacrylic acid (MAA) terpolymer, which was quite difficult by conventional pyrolysis–gas chromatography (Py–GC) mainly because of highly polar nature of MAA moiety, was performed by two-step (double-shot) reactive Py–GC. In this method, the MAA units were converted into methyl methacrylate (MMA) ones, which are readily depolymerize, by tetramethylammonium acetate (TMAAc) in the first step in the microfurnace pyrolyzer. Pyrolysis of the derivatized terpolymer sample was then carried out at 600 °C. Prior to the measurement, the sample was dissolved in THF and premixed with TMAAc to enhance the derivatization efficiencies between the sample and the reagent. The reaction conditions for derivatization were also settled experimentally at 200 °C for 10 min. The pyrogram obtained by this procedure showed some major peaks such as butene, butanol, butyl acrylate, and butyl methacrylate for BA, methyl acrylate and methyl methacrylate for MMA, and styrene and α -methylstyrene for St. Based on the relative peak intensities of these characteristic products detected by a flame ionization detector, the terpolymer composition (mol%) was estimated to be St/BA/MAA = 29.9/33.1/37.1, which was almost identical with the feed composition (St/BA/MAA = 30/33/37) with excellent relative standard deviations less than 0.25%.

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1. Introduction

Pyrolysis–gas chromatography (Py–GC) is widely used for compositional analysis of copolymers [1,2]. However, the analysis of a copolymer sample containing highly polar monomers with a free carboxyl group such as methacrylic acid is generally difficult by using conventional Py–GC because the sample frequently degraded into highly polar pyrolysates and/or intractable products by dehydration condensation during pyrolysis as shown in Fig. 1.

It is well-known that derivatization often improve chromatographic separation and detection of the compounds that are usually not suitable for the direct chromatographic analysis [3]. Typical derivatization reactions involve the conversion of a polar functional group such as the free carboxyl acid into the corresponding alkyl ester. This conversion reduces the polarity of the compound to obtain better resolution and detection in the chromatographic separation. Furthermore, in the case of Py–GC, the derivatization

of a sample polymer often causes much improved efficiency and selectivity of the pyrolysis reaction [4].

For instance, the pyrolysis of a polymer sample in the presence of an organic alkali, typically tetramethylammonium hydroxide $[(CH_3)_4NOH; TMAH]$, often provides a simplified pyrogram. The observed peaks are mainly methyl derivatives of the constituent monomer units in the polymer samples, especially for polyesters and polycarbonates. This procedure is generally called thermally assisted hydrolysis and methylation (THM). The THM reaction linked to GC, THM–GC has been successfully applied to the chemical characterization of a number of synthetic and natural products, including resins, lipids, waxes, wood products, soil sediments, and microorganisms [4–6].

In recent years, a new micro reaction sampler which facilitates the THM reaction of intractable condensation polymers at an elevated temperature in a sealed glass capsule was developed for a microfurnace Py–GC [7]. The function of the sampler was demonstrated through the THM–GC analysis of polycarbonate and polyamide in the presence of TMAH. The closed system accelerated the THM reaction because the reactants were confined within a sealed glass capsule for a long period under a relatively high

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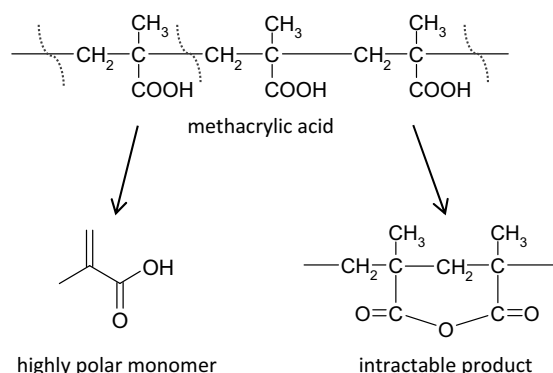


Fig. 1. Typical pyrolysis reaction of poly(methacrylic acid).

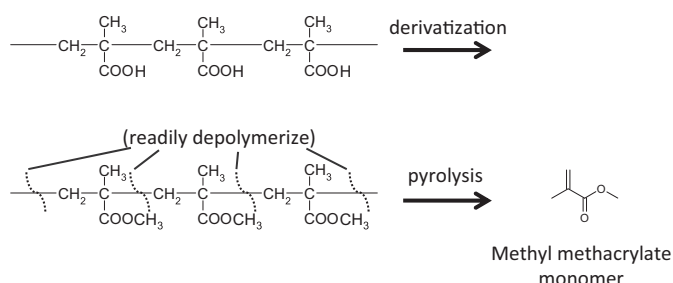


Fig. 2. Probable reaction in two-step reaction pyrolysis of methacrylic acid sequence in polymer chain.

pressure condition compared to the conventional THM-GC using the open system.

In addition, Hardell and Nilvebrant [8] reported that THM-GC technique using tetramethylammonium acetate $[(CH_3)_4N^+ CH_3COO^-; TMAAc]$ as a methylating reagent permitted the rapid and highly sensitive detection of free fatty acids in various lipid mixtures as their methyl esters on the resulting chromatograms. TMAAc was shown to be a selective reagent for derivatization with the ability to methylate fatty acids and their salts without any ester exchange reaction of fatty acid esters. This technique was also applied to the direct compositional analysis of a series of fatty acids and polyphenols contained in wood samples [9], and the determination of terephthalic acid occluded in solid decomposition products obtained from the hydrothermal recycling process of poly(ethylene terephthalate) [10].

On the other hand, stepwise Py-GC in the presence of TMAH at different temperatures was applied to the determination of the end group functionalities of polystyrene macromonomers with methacryloyl (ML) end groups [11]. In this case, stepwise pyrolysis using a two-stage furnace pyrolyzer consisting of two independent furnaces was utilized to decompose the ML end group moieties hydrolytically into their methyl derivatives such as methyl methacrylate (MMA) at 250 °C and then pyrolyze the polystyrene main chains thoroughly at 650 °C. The concentration of the ML end groups was determined by comparing the peak intensity of MMA observed in the former pyrogram with those of the characteristic products formed from the polystyrene main chain in the latter pyrogram.

In this work, precise compositional analysis of a styrene (St)/butyl acrylate (BA)/methacrylic acid (MAA) terpolymer was performed by two-step (double shot) reactive Py-GC. In this method, through the reaction with the organic alkali reagent at around 200 °C the polar MAA units in the terpolymer sample were first converted to MMA units, which are readily depolymerize into MMA monomer during pyrolysis, as shown in Fig. 2. The

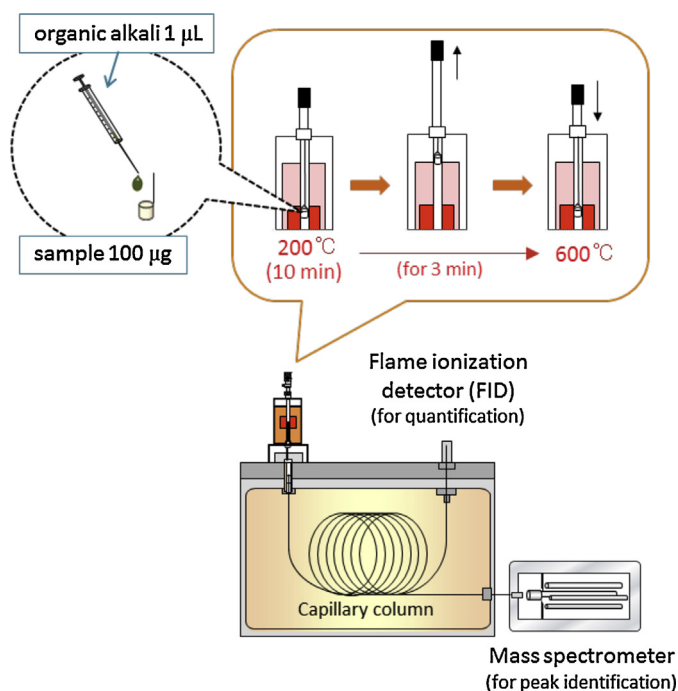


Fig. 3. Schematic diagram of two-step reactive Py-GC system.

converted sample (St/BA/MMA terpolymer) was then pyrolyzed at higher temperature to obtain a specific pyrogram consisting of characteristic products of each monomer unit, of which yields were interpreted in terms of the terpolymer composition. Some basic conditions of this procedure, such as the selection of the organic alkali reagent and the method of sample preparation, were examined to achieve the accurate and precise compositional analysis of the terpolymer sample.

2. Experimental

2.1. Sample and reagents

An industrially available terpolymer sample in powdered form was used as received. The monomer composition of the terpolymer in feed was St/BA/MAA = 30/33/37 (molar ratio). TMAH and TMAAc supplied by Sigma–Aldrich were used as the derivatization reagents. TMAH methanol solution (2.9 M) was used as purchased, while TMAAc methanol solution (3 M) was prepared by dissolving it into methanol (super dehydrated grade, Wako Pure Chemical Industries). Tetrahydrofuran (THF) was purchased from Wako Pure Chemical Industries and used as received.

2.2. Conditions for two-step reactive Py-GC

Fig. 3 shows the schematic diagram of the two-step reactive Py-GC system. A vertical microfurnace pyrolyzer (Frontier Lab, PY-2020iD) was directly attached to a gas chromatograph (Agilent, HP 6890) equipped with a flame ionization detector (FID) set at 320 °C, which was suitable for quantification of the components on the chromatograms. About 100 µg of the powdered terpolymer sample was placed into a sample cup, and then 1 µL of the organic alkali solution was added. Alternatively, the polymer sample was dissolved in THF (100 mg mL⁻¹), an aliquot of the solution (10 µL) was then mixed with the TMAAc solution (10 µL) and stirred well using a vortex mixer in a microtube and finally 2 µL of the mixed solution was put in the sample cup. The cup containing the sample and the reagent was inserted into the pyrolyzer and heated

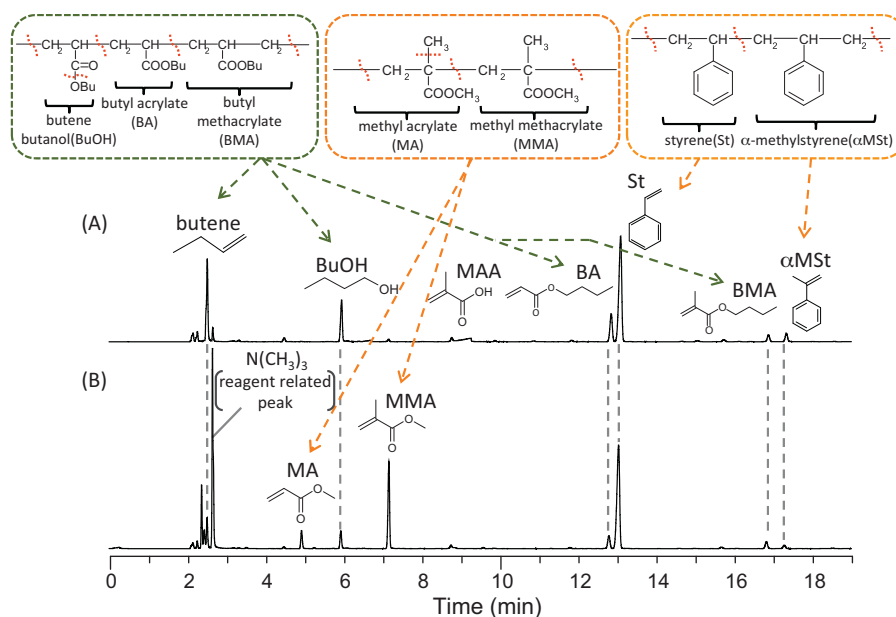


Fig. 4. Pyrograms of the powdered terpolymer sample obtained by (A) conventional Py–GC without addition of any organic alkali, and (B) two-step reactive Py–GC in the presence of TMAH.

at 200 °C for 10 min. These conditions were empirically settled to obtain almost quantitative derivatization with little contribution of undesirable side reaction. In this step, MAA units in the sample could be converted to MMA units.

The cup was then pulled up at the waiting position of pyrolyzer near room temperature, and finally inserted again into the heated center of the pyrolyzer raised at 600 °C (typical temperature for Py–GC measurements of polymer samples [2]) for pyrolysis under the flow of helium carrier gas (50 mL min^{−1}). The pyrolysis products were transferred to the injection port of GC at 320 °C through the Py/GC interface also set at 320 °C. A part of the flow (1 mL min^{−1}) reduced by the splitter was introduced into a metal capillary column (Frontier Lab Ultra ALLOY⁺-5, 30 m × 0.25 mm i.d., coated with 1.0 μm film thickness of 5% diphenyl–95% dimethyl polysiloxane stationary phase) with 83 kPa head pressure. The column temperature was initially set at 50 °C for 3 min, then programmed to 100 °C at a rate of 10 °C min^{−1}, held for 7 min and finally raised to 300 °C at a rate of 10 °C min^{−1}.

Identification of the peaks on the chromatograms was carried out mainly using a GC–MS system (Shimadzu GCMS-QP2010plus) to which the pyrolyzer was directly attached. An electron ionization mass spectrum was obtained with the mass scan range of *m/z* 15–600 at 1250 amu/s. The temperature of the GC/MS interface and the ion source were 250 and 230 °C, respectively.

3. Results and discussion

Fig. 4 shows the typical pyrograms of the powdered terpolymer sample obtained by the conventional Py–GC without addition of any organic alkali (A), and by two-step reactive Py–GC in the presence of TMAH (B), along with the possible origins of the main products. In the pyrogram obtained without derivatization at 600 °C (A), the products reflecting BA and St units in the polymer chain, such as butene, butanol (BuOH), butyl acrylate (BA) and butyl methacrylate (BMA) for BA, and styrene (St) and α-methylstyrene (αMSt) for St, respectively, were clearly observed. However, only a broad peak of methacrylic acid (MAA) was detected for MAA moiety. On the other hand, in the pyrogram obtained under the two-step reactive pyrolysis conditions (B), methyl acrylate (MA) and methyl methacrylate (MMA) can be clearly observed as the

key products of MAA moiety through the derivatization into MMA units. In both pyrograms, products with larger molecular weight were hardly detected after the elution of αMSt.

The chemical composition of the terpolymer was then determined on the basis of the pyrogram obtained under the two-step reactive pyrolysis. Here the terpolymer composition was calculated by using the intensities of the characteristic peaks as follows:

$$\text{St content (mol\%)} = \frac{\sum P_{\text{St}}/\text{ECN}}{\sum (P_{\text{St}}/\text{ECN}) + \sum (P_{\text{BA}}/\text{ECN}) + \sum (P_{\text{MAA}}/\text{ECN})}$$

$$\text{BA content (mol\%)} = \frac{\sum P_{\text{BA}}/\text{ECN}}{\sum (P_{\text{St}}/\text{ECN}) + \sum (P_{\text{BA}}/\text{ECN}) + \sum (P_{\text{MAA}}/\text{ECN})}$$

$$\text{MAA content (mol\%)} = \frac{\sum P_{\text{MAA}}/\text{ECN}}{\sum (P_{\text{St}}/\text{ECN}) + \sum (P_{\text{BA}}/\text{ECN}) + \sum (P_{\text{MAA}}/\text{ECN})}$$

where P_{St} , P_{BA} and P_{MAA} are the observed intensities of peaks reflecting the corresponding monomer components (St and αMSt for St, butene, BuOH, BA and BMA for BA, and MA and MMA for MAA, respectively), and ECN is effective carbon number of each product for FID [12]. The estimated compositions (mol%) for Fig. 4(B) were St/BA/MAA = 34.5/24.7/40.9 as shown in Table 1. By using TMAH, the observed composition of BA (24.7%) was much smaller than the feed composition (33%). In addition, the reproducibility of the measurement was insufficient (relative standard deviation, RSD, was 10.4% for BA for three repeated runs). Because of the high

Table 1

Terpolymer composition estimated by two-step reactive Py–GC under various conditions.

Condition (sample, reagent)	Composition [mol%] (relative standard deviation, RSD) ^a		
	St	BA	MAA
Powder, TMAH	34.5 (0.96)	24.7 (10.4)	40.9 (6.9)
Powder, TMAAc	32.1 (0.82)	39.3 (2.6)	28.6 (4.3)
Solution, TMAAc	29.9 (0.02)	33.1 (0.24)	37.1 (0.20)
Feed composition	30	33	37

^a For three repeated runs.

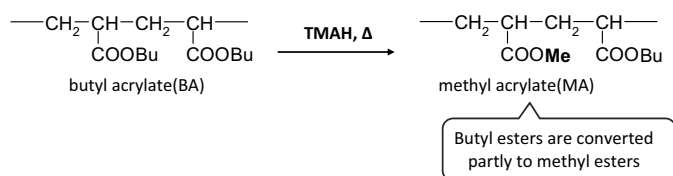


Fig. 5. Partial transesterification of butyl acrylate into methyl acrylate by TMAH.

reactivity of TMAH, transesterification competitively occurs during the derivatization. In this case, TMAH might convert not only MAA to MMA but also partly BA into MA, as shown in Fig. 5. Since MA was attributed to MAA in the compositional analysis, the probable transesterification should cause to underestimate the BA content (and to overestimate the MAA content).

To control the undesirable transesterification reaction, TMAAc was then used as the derivatization reagent which is known to react selectively with free carboxyl groups, because of its weaker basicity compared to TMAH [7]. Fig. 6 shows the pyrogram of the powdered terpolymer sample obtained by two-step reactive Py-GC in the presence of TMAAc. Because the transesterification was restrained by using TMAAc, the peak intensity of MA drastically decreased compared with that in Fig. 4(B) using TMAH. The small amount of MA formed in this case should be derived from the MMA units in the converted polymer chains. It was also confirmed by using a standard BA homopolymer that BA was not transformed into MA under the reactive pyrolysis conditions in the presence of TMAAc. However, the calculated composition from the pyrogram in Fig. 6 (St/BA/MAA = 32.1/39.3/28.6 as shown in Table 1) still deviated from the feed composition. In particular the MAA content was underestimated, probably due to the insufficient derivatization of MAA to MMA (a broad and minor peak of MAA was still observed in Fig. 6). In the case of solid polymer sample the derivatization reaction in the heterogeneous (solid/liquid) phase would be difficult to proceed uniformly and completely. Fairly yield (ca. 7% among the products from BA moiety, as shown in Table 2) of BuOH, which should be produced with hydrolysis reaction, also suggested the incomplete methylation of

Table 2

Reactive yield of butanol observed by two-step reactive Py-GC in the presence of TMAAc for different conditions of the terpolymer sample.

Run number	Relative yield (mol%) ^a	
	Powder	Solution
1	7.3	3.7
2	6.3	3.5
3	7.6	3.6
RSD (%)	7.9	2.2

^a Relative yield among the products derived from BA units

MAA units. As shown in Fig. 7, the insufficient derivatization should cause condensation of residual MAA sequences to form water. Not only the adsorbed moisture in the polymer sample, but also the water formed by the condensation could contribute to the hydrolysis reaction to produce BuOH from BA unit.

Finally, to enhance the derivatization efficiency of the polymer sample, the terpolymer sample and the reagent were premixed prior to the two-step reactive Py-GC measurements. The polymer sample was dissolved in THF with TMAAc, and then an aliquot of the solution was put in the sample cup subjected to the measurements. Fig. 8 shows a pyrogram of the sample solution premixed with TMAAc obtained at 600 °C by two-step reactive Py-GC. Under this homogeneous condition, the relative abundance of BuOH was reduced to about 3.5% (Table 2). This decrease in the BuOH yield supports the derivatization efficiency for the solvitized sample was much improved. The estimated compositions of the terpolymer obtained under different conditions are summarized in Table 1. It should be noted that the composition of the terpolymer sample determined from the premixed solution of the sample and the reagent (TMAAc) was in excellent agreement with the feed composition, together with quite high reproducibility less than 0.25% RSD. The observed results demonstrated that accurate and precise compositional analysis of the terpolymer sample containing highly polar carboxylic acid component can be successfully achieved by two-step reactive Py-GC through the optimization of the reaction

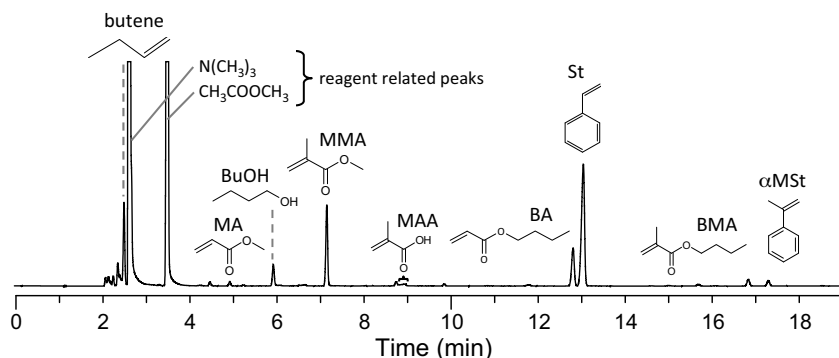


Fig. 6. Pyrogram of the powdered terpolymer sample obtained by two-step reactive Py-GC in the presence of TMAAc.

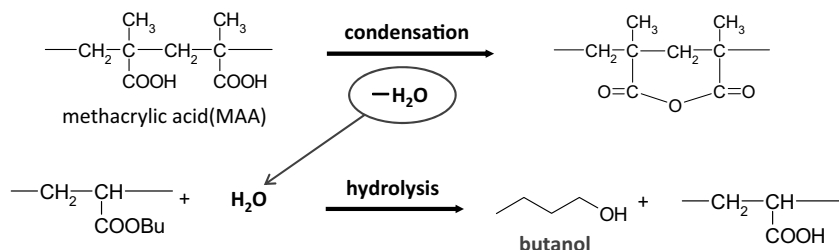


Fig. 7. Possible hydrolysis of BA unit during pyrolysis of the terpolymer sample.

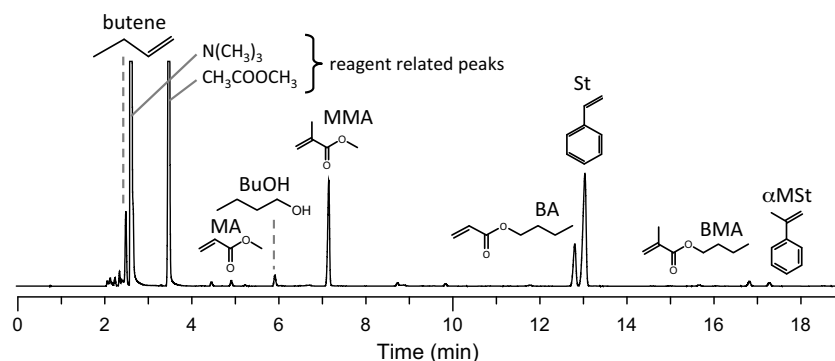


Fig. 8. Pyrogram of the terpolymer sample solution premixed with TMAAc obtained by two-step reactive Py–GC in the presence of TMAAc.

conditions such as the sampling procedure and the selection of the appropriate reagent.

4. Conclusion

A two-step reactive Py–GC analysis was proposed for a terpolymer sample consisting of St/BA/MAA. This terpolymer is quite difficult to determine by conventional Py–GC due to highly polar MAA moiety. In the proposed method, the MAA units were converted into MMA ones, which are readily depolymerize, by an organic alkali reagent in the first step at 200 °C for 10 min, and then the derivatized terpolymer sample was pyrolyzed at 600 °C. From the relative yields of the main products observed in the pyrogram, accurate and precise compositional analysis of the terpolymer sample can be achieved through the selection of the appropriate methylating reagent (TMAAc) and the preparation of the sample solution to enhance the reaction efficiency. The proposed two-step reactive Py–GC method could be suitable for the compositional analyses of various copolymer samples containing highly polar monomer unit such as acrylic and methacrylic acid, when they are intractable for conventional Py–GC measurements. Further study is currently in progress to apply the proposed method for the compositional analyses of various copolymer samples containing acrylic and methacrylic acid units.

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